Laboratory comparison of polyethylene and dialysis membrane diffusion samplers

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ABSTRACT

Diffusion samplers for collecting water samples were constructed from regenerated cellulose dialysis membrane film and low-density, lay-flat polyethylene tubing. Their ability to collect volatile organic compounds and inorganic ions was compared in a laboratory study. Concentrations of vinyl chloride, cis-1,2-dichloroethene, bromochloromethane, trichloroethene, bromodichloromethane, and tetrachloroethene reached equilibrium within 3 days in both types of samplers. Concentrations of Fe and Br reached equilibrium in spiked deionized water and in dialysis membrane samplers within 3 days, but did not attain equilibrium in similar polyethylene samplers within 21 days. Dialysis membrane samplers were studied for leaching of trace elements and sulfide in deionized water. No significant concentrations of Al, As, Ba, Cd, Cr, Fe, Hg, Mn, Ni, and Pb or sulfide were leached out over 7 days. Compared with using a gas-tight syringe to sample the diffusion sampler, clipping the bag and pouring the water sample into a sample vial resulted in slight losses of volatile organic compounds (about 4 percent).

INTRODUCTION

Diffusion samplers have been used to monitor concentrations of volatile organic compounds (VOCs) in ground water (Vroblesky and others, 1996; Tunks and others 2000; Vroblesky and Campbell, 2000; Vroblesky and Hyde, 1997; and Hare, 2000). The use of diffusion samplers is of interest because of the potential cost savings for monitoring VOC concentrations in ground water and the ability of these devices to collect samples in wells over an extended period of time. This sampling methodology is useful for collecting samples to identify VOC concentrations at discrete depths in the open interval of wells in fractured rock aquifers. Because diffusion samplers may eliminate the need to purge water prior to collection of ground-water samples, ground-water monitoring and purge water treatment costs can be reduced.

Diffusion samplers for VOCs are typically constructed of low-density polyethylene (LDPE) lay-flat tubing, which is filled with deionized water, and work on the principle of simple partitioning of VOCs into and across the membrane (Vroblesky and Hyde, 1997). A minimum equilibration time of 14 days typically is recommended for most VOCs, but varies for different organic compounds (Vroblesky, 2001). The equilibration period also depends on temperature, with cooler aquifer temperatures of 10^{o} to 15 ^{o}C requiring a longer equilibrium period than, for instance, normal room temperature of 20^{o} to 25 ^{o}C.

One important distinction of most diffusion samplers constructed from LDPE film is that, although they are satisfactory samplers for many VOCs, they may not be suitable samplers for hydrophilic polar molecules or charged compounds such as inorganic ions, which diffuse into the membrane slowly or not at all (Vroblesky, 2001). Organic compounds with a diameter of about 10 angstroms or larger, such as humic acids, also may not pass through a LDPE membrane. Many semivolatile organic compounds studied by Vroblesky (2001) were poorly sampled with LDPE diffusion samplers. Samplers constructed from LDPE film showed higher concentrations of phthalates inside the sampler than in ambient water probably due to leaching from the polyethylene film. Diffusion samples represent a time-averaged “snapshot” of VOC concentrations in ground water over the preceding 2 to 7 days. It is desirable to keep this period as short as possible to minimize biofouling interferences on the membrane surface.

At most contaminated sites, it is important to collect samples for both inorganic and organic constituents to describe the site geochemistry. Ideally, diffusion samplers could be used to collect samples for both inorganic and organic constituents to describe site geochemistry, instead of using LDPE diffusion samplers to sample for VOC constituents, and submersible pumps or bailers to collect inorganic and nutrient samples. A LDPE diffusion sampler recently developed by USGS scientists for sampling certain inorganic elements in streams (Brumbaugh and others, 1999, 2000) works differently by sequestering divalent metals (Cd, Cu, Ni, Pb, and Zn) in a resin on the LDPE exterior surface. The device consists of a 15 cm strip of LDPE containing oleic acid and Kelex-100[1].

Synthetic and natural membranes have been used in filtration applications for many years. Commonly available membrane filtration materials include regenerated cellulose, cellulose acetate, polysulfone, polycarbonate, polyethylene, and many others. Diffusion samplers constructed from membrane filter material such as cellulose acetate also have been used to collect water samples since at least the 1970s**,** both for inorganic and organic constituents. Hesslein (1976) studied pore water chemistry using a diffusion sampler of this type. Benes (1980) used a dialysis cell containing distilled water to study concentrations of dissolved inorganic ions in streams. Ronen and others (1987) and Margaritz and others (1989) used a similar multi-level dialysis cell sampler with cellulose acetate membrane ends and rigid plastic or glass cells to collect ground-water samples for trace metals, and organic compounds. The individual cells in the latter sampler were used to collect 20 milliliter (mL) samples. Depending on the number and size of cells mounted on the unit, discrete water samples in a range of volumes could be collected. Tunks and others (2000) compared the effectiveness of diffusion samplers constructed from LDPE film to a commercially available polypropylene dialysis cell with 0.2 μm pore diameter cellulose acetate membrane filter ends for collecting VOC samples. Lorah and others (1997) used diffusion samplers constructed from flat Lexan[1] sheet with 0.2 μm polysulfone membrane material (PEEPERS) to collect multiple ground-water samples over a small range of depth. This latter type of sampler was used to collect very small amounts of water (11 mL) for VOC and methane analysis. Brumbaugh and others (2000) developed a semi-permeable polymeric membrane diffusion sampler containing a Hg-sequestering reagent for sampling Hg vapor in air and Hg dissolved in water. Diffusion samplers made from regenerated cellulose dialysis membrane tubing are advantageous because they are permeable to both inorganic and organic compounds, are much more rugged than cellulose acetate membranes, have good chemical compatibility for most environmental applications, and can be constructed to collect larger amounts of sample. The rate of transport of molecules across a semipermeable dialysis membrane is a function of molecular shape, size, charge, fluid temperature, wall thickness, and concentration gradient. Some unanswered questions concerning the effectiveness of dialysis membranes for collecting ground-water samples include potential contamination issues, time-to-equilibrium, and service life in typical field conditions. This study compared the effectiveness of diffusion samplers constructed from regenerated cellulose dialysis membrane and LDPE lay-flat tubing for collecting VOC and inorganic constituents under laboratory conditions.

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[1] Use of brand, trade, or firm names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey

MATERIALS AND METHODS

The LDPE diffusion sampler was constructed from lay-flat 2-mil thickness polyethylene tubing, 10 cm (centimeter) wide (flat) by 15 cm long. One end was closed by heat sealing, then the sampler was filled with 200 mL of laboratory deionized water. The other end was then heat-sealed, leaving no headspace in the bag (fig. 1). The LDPE sampler used in this study differs from the diffusion sampler used by Vroblesky and Hyde (1997) primarily in wall thickness (2 mil (this study) compared to 4 mil (Vroblesky)).

The dialysis membrane diffusion samplers were constructed of 6,000 to 8,000 Daltons nominal molecular weight cutoff (MWCO) regenerated cellulose dialysis membrane material (18 angstroms pore size), purchased from Membrane Filtration Products, Inc.[2] The membrane was Cellu Sep T2, furnished in 10 cm wide by 15 m long rolls, with a nominal wall thickness of 65 μm (dry) or 87 μm (wetted). After wetting, the dialysis membrane sampler volume/length ratio was 31.8 mL/cm., and had a (filled) diameter of approximately 63 mm (millimeters). According to the manufacturer, the membrane material may contain minor concentrations of glycerol, sulfide, Cd, Cr, Cu, Fe, Pb, Ni, and Zn. These chemicals were removed using a decontamination process recommended by the manufacturer, as described below. The membrane material was cut into 20-cm lengths and soaked in deionized water for 15 minutes. The membranes then were rinsed in fresh deionized water and were transferred to a 2-L (liter) beaker containing 10 mM (millimolar) sodium bicarbonate. The contents were maintained, submersed for 30 minutes at 80 ^oC, with occasional stirring. Following this step, the membranes were rinsed in deionized water, transferred to a beaker containing 10 mM ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), and soaked at room temperature for 30 minutes. The membranes then were transferred to a beaker containing deionized water at 80 ^oC and maintained, with occasional stirring, for 30 minutes. The membranes were rinsed in organic-free deionized water, rolled up, and stored, submersed in deionized water containing 0.05 percent sodium azide in the refrigerator until use, for a maximum of 2 days. At the time of sampler construction, the membranes were rinsed again with deionized water to remove the azide preservative. Diffusion samplers were constructed from dialysis membrane by closing one end with a 50-mm plastic clamp and filling the bag with 200 mL of laboratory deionized water. The other end was closed with a plastic clamp of the same type (fig. 1).

The time to equilibrium for both polyethylene and dialysis membrane diffusion samplers was studied using the following VOCs: bromochloromethane (BCM), bromodichloromethane (BDCM), cis-1,2-dichloroethene (cis-DCE), trichloroethene (TCE), tetrachloroethene (PCE), and vinyl chloride (VC). All chemicals were of reagent grade. The VOC spike was made up in methanol containing all analytes, except VC at 1,000 μg/mL (micrograms per milliliter). The VC spike was 2,000 μg/mL.

The equilibration time for VOCs was studied by placing one LDPE and one dialysis membrane sampler each containing deionized water in a series of 3.8-L metal cans with tight-fitting lids (new cans, cleaned and baked overnight at 110 ^oC). The cans were filled completely with deionized water, and given a VOC spike to attain an initial ambient concentration of the target VOC compounds in the can of approximately 100 μg/L. Immediately after the cans were spiked, the lids were affixed, and the cans were inverted to mix the contents. The diffusion samplers were allowed to equilibrate at room temperature (23 ^oC). Five cans were set up

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similarly except for the VOC spikes to serve as laboratory controls. One can from each series was sacrificed for each sampling event: Initial, 3, 7, 14, and 21 days. At each recovery time, samples were collected from the water in the can, and from all diffusion samplers. All samples were transferred to 40-mL VOA vials for GC analysis. Both diffusion samplers and ambient water in the can were sampled in triplicate. The diffusion samplers were routinely sampled by clipping a corner of the bag with scissors and filling 3 VOA vials by carefully pouring, while minimizing aeration of the sample. One set of diffusion samplers was sampled (in triplicate) using a 50-mL gas-tight syringe to determine if any VOC losses occurred by the pouring method. All VOC samples were stored in the refrigerator at 4 ^{o}C prior to GC analysis is for a maximum holding period of 7 days. GC analysis was done by U.S. Environmental Protection Agency method 502.2 (EPA/600/R-95-131).

Iron and Br equilibration times were determined by transferring a weighed amount of each chemical to new 20-L plastic buckets containing 16 L of deionized water, acidified to pH <2 with reagent grade 6 N HNO_3. The iron spike was made up as 0.3994 g reagent grade $FeSO_4 \cdot 7 H_2O$. The Br spike consisted of 0.2085 g of reagent grade sodium bromide. This gave initial concentrations of 5.0 mg/L Fe and 10.1 mg/L Br in the ambient water. The buckets were washed with laboratory detergent and rinsed with deionized water prior to use. Three LDPE and three dialysis membrane diffusion samplers that contained 200 mL of deionized water were placed in each of two buckets containing the Fe and Br spikes; then the lid was affixed. Two additional buckets were set up similarly, but without the Fe and Br spikes, to serve as laboratory controls. The diffusion samplers were allowed to equilibriate at room temperature (23 ^{o}C) for 0, 3, 7, 14, and 21 days prior to sampling. At each equilibration time, one diffusion sampler of each type was sampled by clipping a corner of the bag with scissors and pouring sample contents into a 250-mL polyethylene sample bottle. Samples were stored in a refrigerator at 4 ^{o}C until analysis was complete.

The concentration of dissolved Fe was determined spectrophotometrically by use of the ferrozine procedure described by Stookey (1970). The detection level for this method is 0.01 mg/L Fe. The Br concentration was determined electrometrically by use of a selective ion electrode using an Orion model 94-35 Br electrode. The detection level for Br is 0.1 mg/L.

Potential leaching of sulfide, Al, As, Ba, Cd, Cr, Fe, Pb, Hg, Mn and Ni from decontaminated regenerated cellulose dialysis membrane diffusion samplers was determined by constructing dialysis membrane samplers as previously described, and deploying the samplers in 10.2 cm inside diameter schedule 40 polyvinyl chloride pipe filled with deionized water. After a 7-day period of equilibration at room temperature, a water sample from the dialysis membrane diffusion sampler was transferred to 250-mL polyethylene containers, acidified with 1:1 HNO_3 to pH less than 2, and sent to a contract laboratory for analysis of trace elements by inductively coupled plasma (ICP), (USEPA method 200.7). Sulfide samples were collected in 40-mL VOA vials and preserved with 100 µL (microliters) each of 1 M zinc acetate and 6 N NaOH. Sulfide concentration was determined spectrophotometrically by use of the methylene blue method described by Cline (1969).

The results were evaluated with the Kruskal-Wallis rank sum test or the Student's T-test. The concentration of VOCs in different diffusion samplers over time was not normally distributed. The Kruskal-Wallis test is a nonparametric alternative to a one-way analysis of variance (ANOVA) and does not assume sample normality, as does the one-way ANOVA. The Student's T-test was used to evaluate differences in VOC concentrations between samples taken by clipping and pouring from the diffusion samplers or by using a gas-tight syringe. These differences were normally distributed.

RESULTS

Laboratory tests of diffusion samplers indicated rapid equilibration times for all VOCs studied in both the LDPE and dialysis membrane diffusion samplers. The results for TCE, cis-DCE, and VC are shown in figures 2 to 4, respectively. After equilibrating for 3 days at room temperature, there was no significant difference ($P>0.05$) between the concentrations of TCE, cis-DCE, VC, BCM, BDCM, or PCE in ambient water and VOC concentrations in the diffusion samplers. The VOC concentrations in the LDPE sampler tended to slightly exceed the mean concentrations in the dialysis membrane sampler and the ambient water for the 3- and 7-day sample times, but the differences were not significant at the 95 percent confidence level. Although not shown in figures 2 to 4, the results for BCM, BDCM, and PCE were equivalent to the results shown for the other VOCs. These equilibration times are similar to those published studies reported by Vroblesky (2001), and Vroblesky and Campbell (2000), which used polyethylene diffusion samplers. Ronen and others (1987) reported approximately 70 percent equilibrium for 1,1,1, trichloroethane and 50 percent equilibrium for PCE within 24 hours in the laboratory using pyrex dialysis cells with two different types of membranes.

Equilibration for Fe and Br in the dialysis membrane diffusion samplers was rapid. After 3 days at room temperature, there was no significant difference ($P>0.05$) between concentrations of Fe and Br in ambient water and in dialysis membrane samplers (figures 5 and 6), using the Kruskal-Wallis rank sum test. In contrast, after 21 days of equilibration at room temperature, there was no detectable diffusion of Fe and Br into the LDPE diffusion samplers. These results are similar to reported laboratory equilibrium tests for chloride, nitrate, and sulfate using dialysis cells with 40 angstrom pore diameter cellulose acetate membrane ends (Ronen and others, 1987). In that study, the equilibrium time for chloride and nitrate was less than 24 hours, but sulfate equilibrium time was much longer, approximately 90 hours.

The LDPE sampler developed by Brumbaugh and others (1999) was reported to give good results for estimation of Cu, Ni, Zn, Cd, and Pb concentrations in flowing waters within 4 days, but time-to-equilibrium under static (unstirred) conditions in the laboratory was considerably longer. The effectiveness of the sampler was also reduced at pH ranges of 3.5-6.0, depending on the cation. The LDPE sampler cannot be used to quantify concentrations of anions. The authors deployed a modified LDPE sampler in the field with a sheath of cellulose dialysis tubing (1,000 MWCO) containing deionized water installed over the LDPE sampler. Sampling rates for Cu, Ni, Zn, Cd, and Pb from the sheathed LDPE sampler were similar to laboratory static rates, that is, appreciably less than for samplers deployed in flowing waters. Concentrations of metal ions in deionized water contained in the dialysis tubing were not reported. Other than the MWCO difference, the samples collected from the dialysis portion of the modified Brumbaugh and others (1999) sampler would be expected to be equivalent to those in this study.

Leach test results for Al, As, Ba, Cd, Cr, Fe, Pb, Mn, Hg, Ni, and sulfide concentrations in decontaminated dialysis membrane diffusion samplers after a 7-day equilibration period in deionized water are shown in table 1. When the concentrations shown in table 1 are compared to concentrations of the same constituents in deionized water blanks analyzed by the same contract laboratory, the results indicate that the concentrations of these elements and sulfide were not significantly different ($P>0.05$) from concentrations of these constituents in laboratory deionized water blanks, based on Kruskal-Wallis test.

Results of the comparison between VOC concentrations in samples taken from the diffusion samplers using a gas-tight syringe and by clipping and pouring from the diffusion sampler are shown in figure 7. The concentrations for all VOC compounds tended to be slightly greater when the diffusion samplers were sampled using a gas-tight syringe. The data for the different sampling methods were then compared using a paired T-test. Results indicated that there was a small, but significant, loss of VOCs, or about 4 percent, ($P=0.001$) when the VOA vial was filled by pouring from the diffusion sampler, compared to sampling the diffusion sampler by gas-tight syringe.

DISCUSSION

Diffusion samplers constructed from LDPE tubing and those constructed from regenerated cellulose dialysis membrane gave equivalent VOC concentrations in samples in the laboratory. Concentrations of BCM, BDCM, cis-DCE, TCE, PCE, and VC equivalent to the initial spiked solution were reached in both types of samplers within 3 days. Tests with diffusion samplers constructed of dialysis membrane indicated that Fe and Br concentrations in ambient water reached equilibrium concentrations in the diffusion samplers within 3 days. Diffusion samplers constructed of LDPE tubing, however, were not effective for ionic solutes.

Regenerated cellulose dialysis membrane material is reported to have a slight negative surface charge in waters above pH 3 (Dan Keil, Membrane Filtration Products, personal communication, 2002). This could result in a sampling bias, where cation concentrations in the dialysis sampler might be different than in ambient water. Charge effects were not observed in this laboratory study, however, they should be considered in field trials.

The potential exists for leaching of certain trace elements and sulfide from dialysis membranes, unless a strict and lengthy cleaning process is followed. Dialysis membrane samplers required a lengthy cleaning process before use and careful handling after construction, including refrigeration and storage submersed in a preservative solution. Provided that the membranes were cleaned as recommended by the manufacturer, the concentrations of these contaminants was not a major problem. Potential leaching of contaminants from uncleaned dialysis membrane material was not studied and could be significant. Trace elements other than those analyzed for in this study may be leached from dialysis membranes. Zinc and Cu were not included in the ICP analyses conducted for this study. The use of regenerated cellulose membrane material in varying MWCO ranges could allow for convenient sampling of specific size classes of ions in ground water. This aspect was not considered in this study. The membrane material used in this study had a pore size of 18 Angstroms, which would exclude all but the smallest colloids. Dialysis membranes are available in a variety of sizes and with different molecular weight cutoff limits, which may be useful for collecting other organics, such as humic acids, which was not studied in this investigation. Also, some dialysis membranes are available precleaned at additional cost, which would reduce sampler construction time. Precleaned membranes were not available in the size used in this study. Because regenerated cellulose membranes are utilized for growth by cellulolytic bacteria, there is a real potential for bacterial degradation of the membrane if they are deployed in the field for long periods that is, longer than 1 month. This aspect should be field tested before using dialysis membrane samplers for lengthy environmental sampling. Biofouling of all types of diffusion samplers can occur under certain environmental conditions, such as those in eutrophic, shallow streams. Huckins and others (1996) reported that some reduction in diffusion sampler efficiency occurred when they became colonized by aquatic fungi and periphyton, following lengthy deployment in streams, but the effects of biological growth on diffusion sampler efficiency for sampling VOCs and inorganic compounds in ground-water monitoring wells is largely unknown.

The dialysis membrane diffusion samplers used in this study have similarities to multi-layer diffusion samplers described by Ronen and others (1987), Magaritz and others (1989), and Lorah and others (1997) in that both types of samplers can be used to collect ground-water samples for inorganic and organic substances. Ronen and others (1987) and Magaritz and others (1989) reported using a cellulose acetate membrane with a 40-angstrom nominal pore diameter, which was used to obtain colloid and particulate-free ground-water samples for trace elements and selected organics. The dialysis membrane material used in this study had a nominal pore size of 18 angstroms, which would exclude all but the smallest colloids from the sampler. In contrast with these other samplers, the semi-permeable membrane used in this study was in contact with ambient water on all sides, which potentially would allow shorter equilibrium times. The multi-layer design of these other samplers, and the PEEPERS used by Lorah and others (1997), are well suited for collection of small volumes of sample integrated over short depth intervals (several cm). The tubular bag samplers used in this study, however, collect a larger sample integrated over the length of the sampler.

Diffusion samplers constructed from regenerated cellulose dialysis membrane material potentially have advantages over commercially available polypropylene cylinder diffusion samplers with cellulose acetate membrane filter ends and similar PEEPER type diffusion samplers with rigid sides and membrane filter ends. Dialysis membrane bag samplers can be constructed in any size capacity from a few milliliters to several liters to accommodate different sampling requirements and various well-bore diameters. Additionally, because the entire exposed surface of the dialysis membrane bag is permeable, the time-to-equilibrium for VOCs and inorganic ions should be less than that for diffusion samplers with permeable surfaces on the ends only.

The major advantage of dialysis membrane diffusion samplers over most LDPE samplers is the ability to collect both inorganic and VOC ground water samples without producing large volumes of purge water that must be disposed of or treated. The LDPE sampler described by Brumbaugh and others (1999) is different in that it works by sequestration of selected trace metals in a reagent mixture on the exterior surface of the sampler, so is primarily intended to sample weakly complexed metals in flowing waters. Diffusion samplers potentially can greatly reduce the collection expense for ground water monitoring at many contaminated sites. Because equipment cost for pumps is eliminated, as is purge water produced by conventional ground-water sampling, much of the initially higher cost associated with dialysis membrane sampler construction may be balanced by the potential reduction of costs associated with conventional ground-water sampling. Manpower requirements to collect ground water samples for both inorganic and organic compounds are less with dialysis membrane diffusion samplers than with other sampling methodology.

Another problem is turbidity, introduced during purging and disturbing of ground water in the well casing during sampling. Gibs and others (2000) reported that mobilized particulates larger than 1,000 nanometers, which comprise suspended particulates, can scavenge many trace elements in ground water. If a ground-water sample for inorganic constituents isn't filtered, the concentrations for some regulated trace elements, Al and Fe for example, can be biased upward in unfiltered samples, in comparison with filtered ground water samples. The concentrations of many trace elements are correlated directly with water turbidity (Gibs and others, 2000). This is an important problem if the ground-water compliance monitoring protocol is part of the low-flow unfiltered-sample process described by Puls and Barcelona (1995). The use of dialysis membrane diffusion samplers for collecting ground-water samples should eliminate this uncertainty concerning sampling in wells with high turbidity. Molecules smaller than the size of the membrane pores (MWCO), small colloids and dissolved ions, for example, should be able to pass into the diffusion sampler, but larger particulates will be excluded.

CONCLUSIONS

Diffusion samplers constructed from dialysis membrane material can be used to sample for common VOCs and inorganic ions such as Fe and Br. Diffusion samplers made from polyethylene can be used to sample for VOCs but cannot be used to sample for inorganic ions. Possible contamination of dialysis membrane material with trace elements can effectively be eliminated if a rigorous cleaning procedure is used. Concentrations of VOCs in diffusion samplers constructed of both polyethylene and dialysis membrane material reached equilibrium with surrounding spiked water concentrations within 3 days. Time to equilibrium may effectively be shorter for some VOC compounds. Sampling diffusion samplers by clipping and pouring into a VOA vial resulted in approximately 4 percent loss of VOCs compared to sampling a diffusion sampler with a gas-tight syringe, and transferring the contents to a VOA vial.

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Figure 1. Polyethylene and dialysis membrane diffusion samplers.

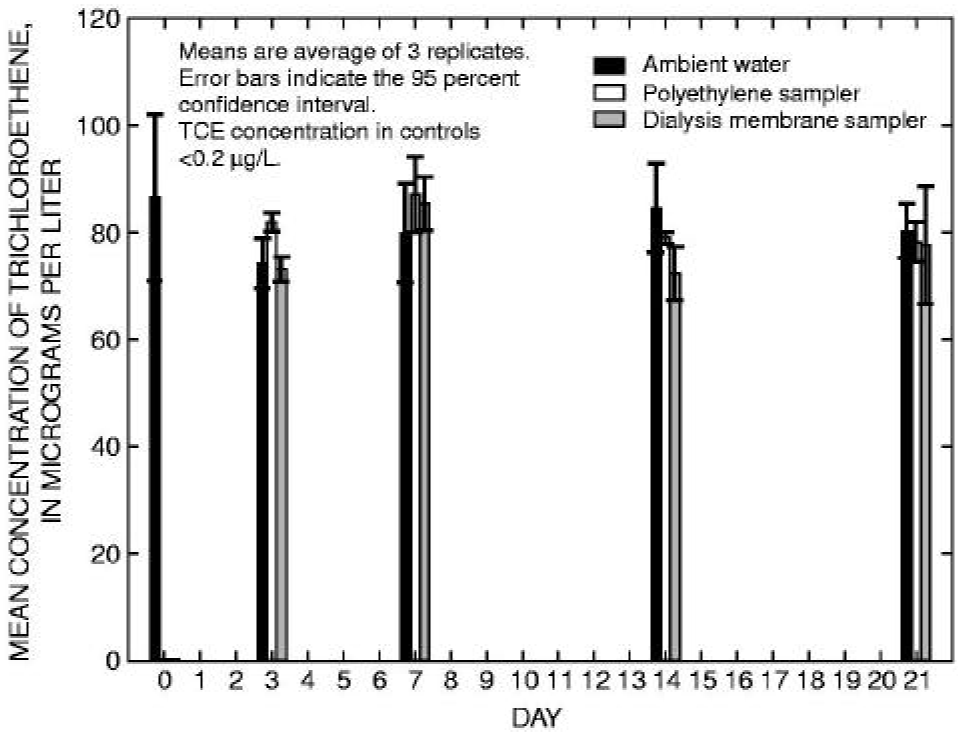

Figure 2. Mean concentration of trichloroethene in ambient water, and in polyethylene and dialysis membrane samplers.

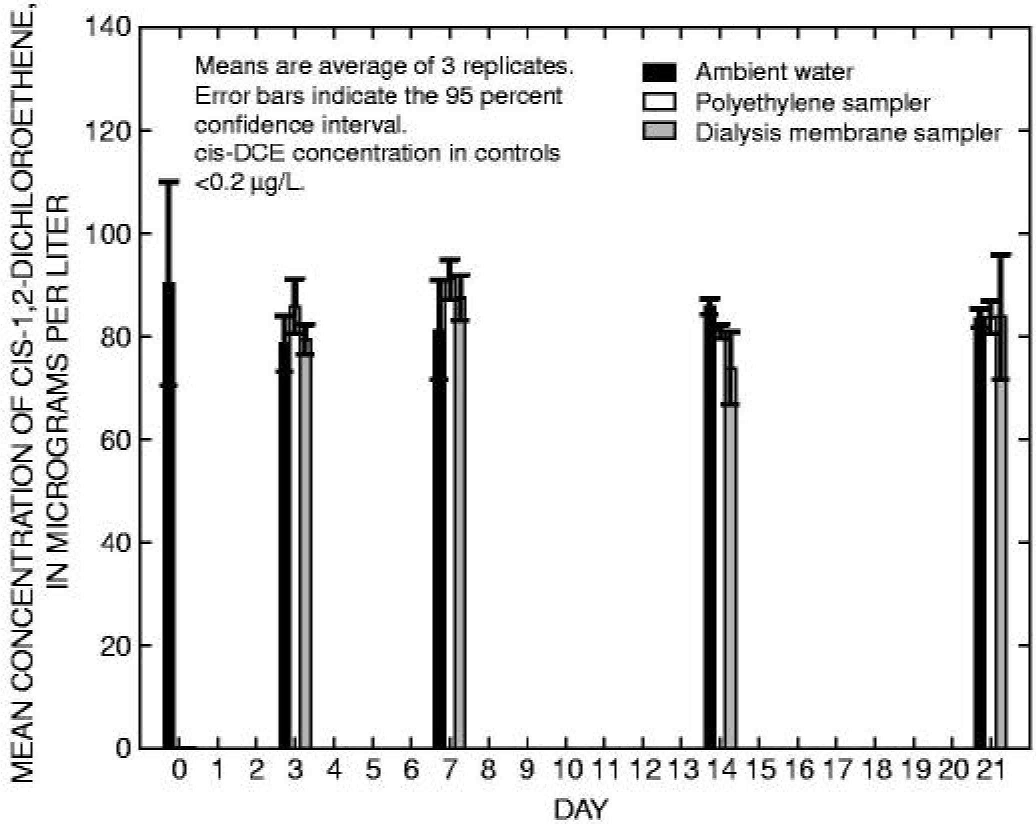

Figure 3. Mean concentration of cis-1,2-dichloroethene in ambient water, and in polyethylene and dialysis membrane samplers.

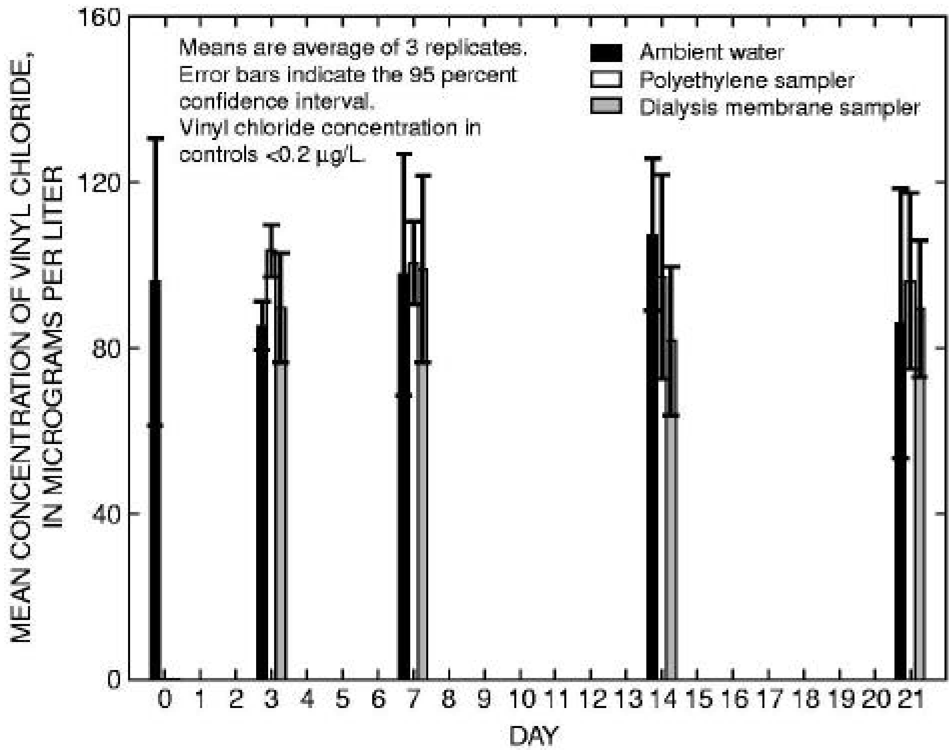

Figure 4. Mean concentration of vinyl chloride in ambient water, and in polyethylene and dialysis membrane samplers.

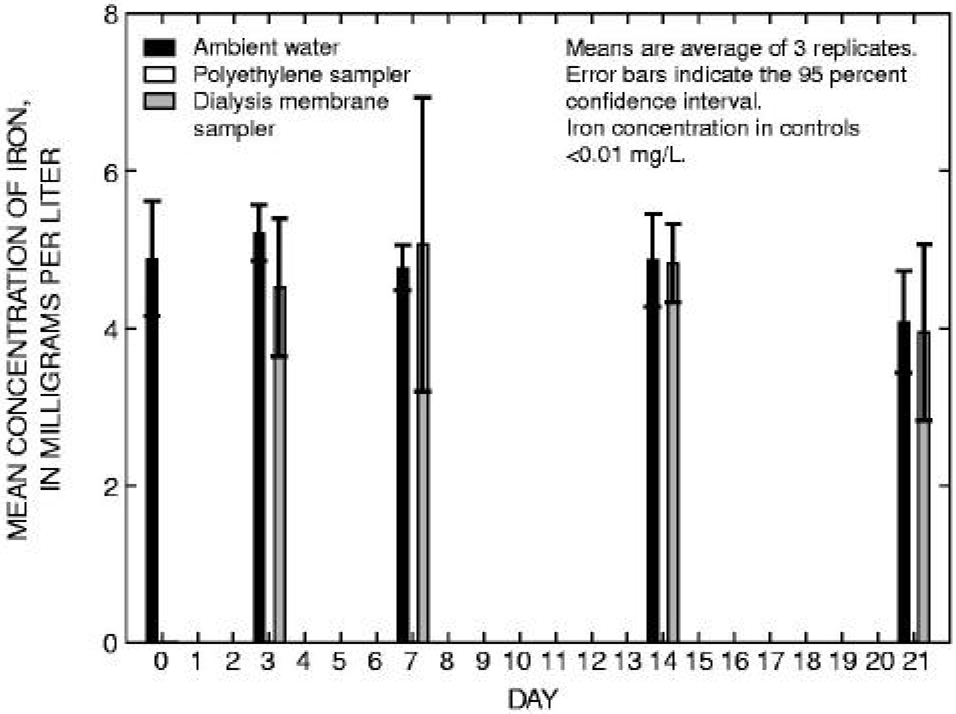

Figure 5. Mean concentration of dissolved iron in ambient water, and in polyethylene and dialysis membrane samplers.

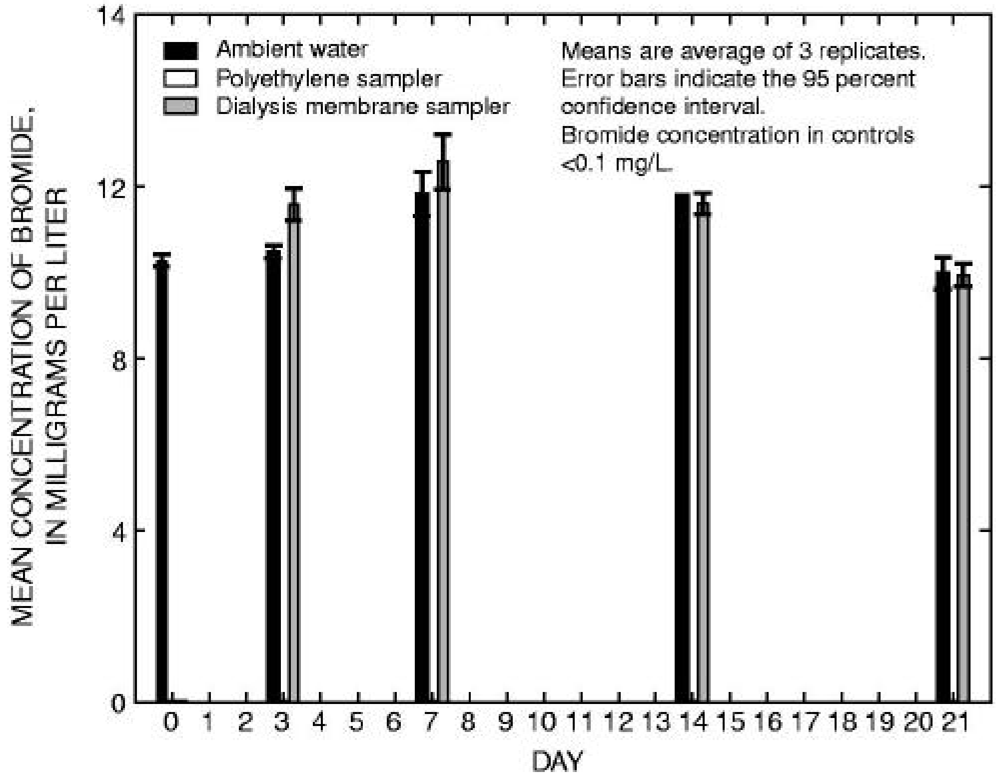

Figure 6. Mean concentration of bromide in ambient water, and in polyethylene and dialysis membrane samplers.

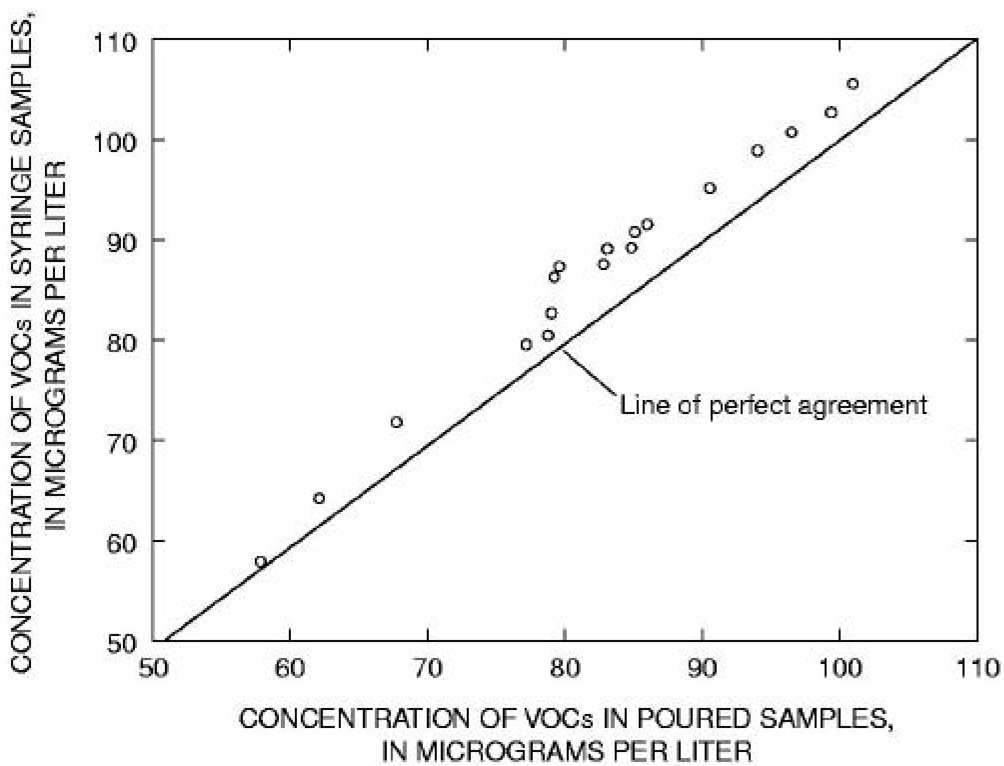

Figure 7. Comparison of VOC concentrations in diffusion samples collected by gas-tight syringe and by clipping and pouring.